AMPHIPHILIC BLOCK COPOLYMER FROM HYDROXYL-TERMINATED POLYMERS FUNCTIONALIZED WITH TEMPO. A NEW SYNTHETIC METHOD USING OXOAMMONIUM SALT[†]

Uriel Márquez-Lamas[1], Tania E. Lara-Ceniceros[1], D. G. Ramírez-Wong[2], Enrique Saldívar-Guerra[2], F. Pérez-Rodríguez[1] José Bonilla-Cruz,*[1],

[1] *Centro de Investigación en Materiales Avanzados (CIMAV), Unidad Monterrey, Av. Alianza Norte 202, Autopista Monterrey-Aeropuerto Km 10, Apodaca, Nuevo León-México, C.P. 66600. E-mail: jose.bonilla@cimav.edu.mx*
[2] *Centro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna 140, Saltillo, Coahuila-México.*

Abstract

This work presents a simple approach for the end-functionalization of hydroxyl-terminated polymers with nitroxide moieties using oxoammonium salts (OS). The functionalization is carried out using only one synthetic pathway in which are found high levels of functionalization (90%). A mechanism for the functionalization with TEMPO moieties using OS is proposed in which the formation of peroxide groups is suggested. The structures of the functionalized polymers are characterized in detail by ^{1}H NMR, ^{13}C NMR, DQF-COSY, and HETCOR. Bifunctional macroalkoxyamines are used to demonstrate how to extend the polymer chain for the synthesis of amphiphilic triblock copolymers by polymerizing St in a second block mediated by a nitroxide radical which provides the block length control.

Introduction

Great interest has been focused on functional polymers as building blocks for the synthesis of block and graft copolymers.[1] In particular, amphiphilic block copolymers are very attractive materials from both the scientific and the industrial point of view due to their hydrophobic/hydrophilic behavior.[2] In particular, the synthesis of triblock copolymers such as PSt-b-PPG-b-PSt, PSt-b-PDMS-b-PSt, or PSt-b-PEG-b-PSt using a prepolymer of poly(propyleneglycol) (PPG), polydimethylsiloxane (PDMS), or poly(ethylene glycol) (PEG), respectively, previously functionalized at the ends of each chain with nitroxide moieties, in the presence of styrene (St) monomer have been less studied. On the other hand, nitroxides are stable free radicals that in the presence of a specific counter-ion could lead to oxoammonium salts (OS).[3] This kind of salts are powerful, selective, and nonmetallic oxidants extensively used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.[4] But in the presence of a base (e.g., triethylamine, Et3N), its chemistry of oxidation radically changes to a chemistry of functionalization, which is not an obvious result. Nowadays, all strategies of synthesis developed to obtain amphiphilic diblock or triblock copolymers of PPG, PEG, or PDMS with PSt, using bifunctional macroalkoxyamines and St involve numerous synthetic pathways and sophisticated methods of purification. In this work we show a simple, direct, and general approach for the end-functionalization of hydroxyl-terminated polymers (PDMS, PEG, and PPG) with nitroxide moieties using OS [Br-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)] in the presence of Et3N in solution. Notice that, as far as we know, the OS has not been used before for this end in polymers.

Experimental

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Synthesis of Oxoammonium Bromide Salt: Br-TEMPO. Bromine was added to a solution of TEMPO. A brown solid (Br-TEMPO) was formed instantaneously and was purified by a Soxhlet extraction system using CCl_4. Br-TEMPO salt was dried over vacuum at room temperature overnight.

Synthesis of the Bifunctional Macroalkoxyamines. Three kinds of macroalkoxyamines were synthesized. The reaction conditions for the functionalization of PPG (purified on a chromatographic column to remove the antioxidants), PEG, and PDMS with nitroxide moieties using OS are summarized in Table 1. Functionalize polymers were washed with THF, filtered and finally purified in a chromatographic column.

Table 1. Reaction conditions for the functionalization of hydroxyl-terminated polymers with TEMPO moieties, using oxoammonium salt (OS, Br-TEMPO).

Polymer	Substrate	Amount (g)	$\bar{M}_n$ (Da)	OH (mol)	OS (mol)	Et_3N (mol)	CH_2Cl_2 (mL)	Time (h)	Temp. (°C)
PPG-T	PPG	25	3500	0.041	0.041[a]	0.045	100	12	60
PEG-T	PEG	1	600	0.004	0.008[b]	0.008	2.6	12	60
PDMS-T	PDMS	10	4250	0.005	0.01[b]	0.02	10	24	40

[a] Using a stoichiometric relation (1:1) of OH groups:OS and PPG purified (without antioxidant); [b] Using an excess of OS (1:2) with respect to PEG or PDMS without purification.

Synthesis of Amphiphilic Triblock Copolymers. In order to demonstrate the extension of the polymer chain, we decided to use two bifunctional macroalkoxyamines for the synthesis of triblock copolymers of PSt-b-PPG-b-PSt and PSt-b-PDMS-b-PSt, respectively, by polymerizing St in a second block mediated by a nitroxide radical. Table 2 summarizes the reaction conditions for each case. The reaction mixture was purified in methanol twice, and the polymer obtained was characterized by SEM or TEM.

Table 2. Polymerization conditions used for the synthesis of amphiphilic triblock copolymers at 130 °C in toluene.

Copolymer	Bifunctional macroalcoxiamine		Amount (g)	Toluene (mL)	St		T (h)
	Type	$\bar{M}_n$(Da)			(g)	(mL)	
PSt-*b*-PPG-*b*-PSt	PPG-T	4392	0.5	80	2.07	1.86	14
PSt-*b*-PDMS-*b*-PSt	PDMS-T	6170	5	20	15	13.5	4

Results and Discussion

Proposed Reaction Mechanism. The simple synthetic route, to obtain functionalized polymers at the ends of each chain with TEMPO moieties using OS (Br-TEMPO) is shown in Figure 1. The reaction mechanism proposed to obtain (2) involves a radical substitution by a free-radical process. In this reaction, it is assumed that the hydrogen atoms presents in the hydroxyl groups at the ends of each polymeric chain can be abstracted by a bromine radical generating hydrobromic acid (HBr). Thus, an oxygen-centered radical site at the ends of each chain is formed,[5] which is then quickly capped by the nitroxide radical in order to form (2). The HBr formed is trapped by Et_3N to form triethylamine hydrobromide

(Et$_3$NHBr). In a second stage, amphiphilic block copolymer (3) is formed using (2) in the presence of St and solvent at 130 °C during 14 h.
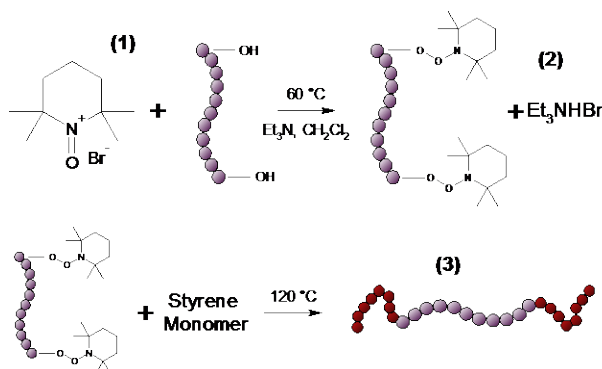

Figure 1. Schematic representation proposed of the functionalization of hydroxylterminated polymers with TEMPO using OS (Br-TEMPO) and their use in the synthesis of block copolymers.

Functionalization of Hydroxyl-Terminated Polymers with TEMPO Using Oxoammonium Salts (Br-TEMPO): FTIR Analysis. Unmodified PPG and PPG-T were characterized in detail. PPG: 3509, 1342, and 662 cm^{-1} corresponding to stretch vibrations (O-H) of the intermolecular hydrogen bonding, CH-OH and out-of-plane OH bonding of the bend O-H group, respectively. In the region of 2867–2962 cm^{-1} symmetrical (v_s) and asymmetrical (v_{as}) stretching vibrations of C-H, corresponding to CH$_2$ and CH$_3$ groups, were observed. A strong absorption band at 1094 cm^{-1} was attributed to a stretching vibration from C-O-C. Also, a stretching vibration of C-O of primary alcohol was observed at 1012 cm^{-1}. In case of PPG-T new bands at 3122 and 2759 cm^{-1} was attributed to -CH2- and -CH3 groups of the piperidine ring from TEMPO. Also, at 724 and 614 cm^{-1} were observed and were attributed to N-O bonds of the piperidine ring from TEMPO and NO-OC bonds (peroxide groups), respectively.[6] Notice that the broad vibration band at 3509 cm^{-1} from PPG is not present in the PPG-T spectra which, jointly with the vibration at 614 cm^{-1}, suggests that the functionalization was successful.

NMR Analysis. The structure of the unmodified and functionalized polymers was evidenced by NMR. In the case of PEG unmodified, the polymer only exhibit typical resonances centered at δ=3.2ppm attributable to hydroxyl groups from the alcohol –CH$_2$-OH of the hydroxyl terminated PEG. At δ=3.53ppm was observed a resonance attributed to two protons of the –OCH$_2$– group.[7]. PPG showed typical resonances centered at δ=1.1, 3.4 and 3.63 attributed to –CH$_2$–, –CH–, and –CH$_3$ groups, respectively. In the PEG-T structure, new resonances were observed centered at δ=1.36, 1.63, 1.81, and 2.15ppm attributed to –CH$_2$– groups of the piperidine ring from TEMPO and resonances centered at δ=0.3 and 0.2ppm were attributed to –CH$_3$– groups from TEMPO. In the case of PPG functionalized with TEMPO was observed the same resonances that in the case PEG-T. All these new assignments were confirmed by ^{13}C NMR, DQF-COSY, and HETCOR.

Functionalization efficiency. Based in the experimental chemical shifts, the new chemical composition was estimated and the degree of functionalization. The chemical shift in the range of δ=1.83–2.15 (-CH$_2$-) was considered for the estimation of the final chemical

composition in all cases (PPG-T and PEG-T). The efficiencies of functionalization obtained by ^{1}H NMR and by titration with iodine (as indirect test) are shown in Table 3. In Table 3, we can observe that the key to obtain high values of functionalization (*f*) is to remove the antioxidants present in the prepolymer prior to functionalization. The degree of functionalization was calculated according to the Equation 1

Ec. 1   degree of functionalization $= \dfrac{\text{amount of nitroxide from } ^1\text{H NMR}}{\text{amount of OH capable of functionalization}} \times 100$

Polymer	Amount of OH available for functionalization (mol)	Nitroxide content (by ^{1}H NMR) (mol)	Degree of functionalization (%)	
			^{1}H NMR	Titration
PPG-T	0.041	0.0369	90	88
PEG-T	0.004	0.0036	90	89
PDMS-T	0.005	0.0024	50	45

GPC Analysis. In order to demonstrate the application of the previously functionalized polymers (PPG-T, PEG-T, and PDMS-T) as bifunctional macroalkoxyamines in the controlled chain extension polymerizing St monomer as second block and confirm the possibility of synthesizing block copolymers, we decided to study for the PPG-T and PDMS-T, the chain extension by GPC to obtain block copolymers of PSt-b-PPG-b-PSt and PSt-b-PDMS-b-PSt. Thus, Table 4 shows the gradual shift of the molecular weights towards high molecular weights exhibiting low polidispersities, indicating that the chains of polymer were growing in a controlled fashion.

Table 4. The GPC analysis shows the increment of molecular weights to higher and narrow polidispersities.

	PPG-OH	PPG-T	PSt-b-PPG-*b*-PSt	PDMS-OH	PDMS-T	PSt-*b*-PDMS-*b*-PSt
$\bar{M}_n$(Da)	3500	4392	5967	4250	6170	7374
PD	1.03	1.1	1.37	1.5	1.6	1.64

Morphology. In the figure 2A is observed a microphase segregation (as in HIPS case) reveling spherical morphologies. The sample was not stained, thus the continuous phase is attributed to PSt domains. In the figure is observed that spheres formed presents similar sizes, this because the control that the nitroxide provides. In the figure 2B, the same sample was annealed with toluene vapors by 10 min at room temperature the spherical, domains showed a rearrangement, exhibiting a more ordered packing and, as a consequence, a smaller distance between them.
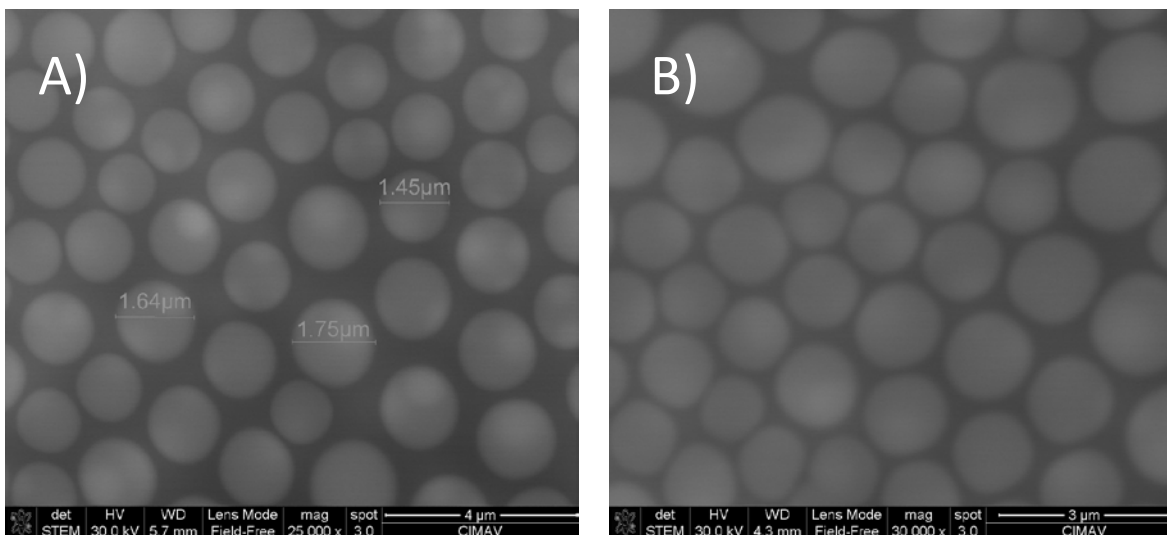
Figure 2. SEM images. A) PSt-b-PPG-b-PSt and SEM analysis obtained by casting (THF). B) PSt-b-PPG-b-PSt and SEM analysis (after annealing with toluene).

Conclusions

Hydroxyl-terminated polymers can be functionalized using oxoamonium salts (Br-TEMPO) giving as result a bifunctional macroalcoxiamine which was experimentally corroborated by FT-IR, ^{1}H NMR, and ^{13}C NMR. This macroalcoxiamine was employed in presence of styrene monomer to the synthesis of aphiphilic block copolymers. The oxoamonium salts are strong candidates to the functionalize polymers with OH groups situated at the end of the polymeric chain. Was proposed a new mechanism of functionalization in where peroxide groups are formed. Also was demonstrated that bifunctional macroalcoxiamine in presence of styrene monomer can produce block copolymers, this was demonstrated by GPC in where obtain narrow polidispersities and higher molecular weights. Finally, the morphology of the block copolymer was evidenced as spherical morphologies.

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